SLOVENSKI STANDARD

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Materiali in predmeti v stiku z ġivili - Snovi v polimernih materialih, katerih koncentracija je omejena - 8. del: Doloļevanje izocianatov v polimernih materialih

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 8: Determination of isocyanates in plastics

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Beschränkungen unterliegen - Teil 8: Bestimmung von Isocyanaten in Kunststoffen

Matériaux et objets en contact avec les denrées alimentaires - Substances dans les matieres plastiques soumises a des limitations - Partie 8 : Détermination des isocyanates dans les matieres plastiques

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67.250	Materiali in predmeti v stiku z živili	Materials and articles in contact with foodstuffs

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EUROPEAN STANDARD

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English version

Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 8: Determination of isocyanates in plastics

Matériaux et objets en contact avec les denrées alimentaires - Substances dans les matières plastiques soumises à des limitations - Partie 8 : Détermination des isocyanates dans les matières plastiques

Werkstoffe und Gegenstände in Kontakt mit Lebensmitteln - Substanzen in Kunststoffen, die Beschränkungen unterliegen - Teil 8: Bestimmung von Isocyanaten in Kunststoffen

This European Standard was approved by CEN on 24 March 2004.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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Contents

Foreword

This document (EN 13130-8:2004) has been prepared by Technical Committee CEN/TC 194 “Utensils in contact with food”, the secretariat of which is held by BSI.

This document was prepared by Subcommittee SC1 of TC 194 as one of a series of analytical test methods for plastics materials and articles in contact with foodstuffs.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2004, and conflicting national standards shall be withdrawn at the latest by November 2004.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

This standard is intended to support Directives 2002/72/EC [1], 89/109/EEC [2], 82/711/EEC [3] and its amendments 93/8/EEC [4] and 97/48/EC [5], and 85/572/EEC [6].

At the time of preparation and publication of this part of EN 13130 the European Union legislation relating to plastics materials and articles intended to come into contact with foodstuffs is incomplete. Further Directives and amendments to existing Directives are expected which could change the legislative requirements which this standard supports. It is therefore strongly recommended that users of this standard refer to the latest relevant published Directive(s) before commencement of a test or tests described in this standard.

EN 13130-8 should be read in conjunction with EN 13130-1.

Further parts of EN 13130, under the general title *Materials and articles in contact with foodstuffs - Plastics substances subject to limitation*, have been prepared, and others are in preparation, concerned with the determination of specific migration from plastics materials into foodstuffs and food simulants and the determination of specific monomers and additives in plastics. The other parts of EN 13130 are as follows.

Part 1: *Guide to test methods for the specific migration of substances from plastics to foods and food simulants and the determination of substances in plastics and the selection of conditions of exposure to food simulants*

Part 2: *Determination of terephthalic acid in food simulants*

Part 3: *Determination of acrylonitrile in food and food simulants*

Part 4: *Determination of 1,3-butadiene in plastics*

Part 5: *Determination of vinylidene chloride in food simulants*

Part 6: *Determination of vinylidene chloride in plastics*

Part 7: *Determination of monoethylene glycol and diethylene glycol in food simulants*

Part 9: *Determination of acetic acid, vinyl ester in food simulants*

Part 10: *Determination of acrylamide in food simulants*

Part 11: *Determination of 11-aminoundecanoic acid in food simulants*

Part 12: *Determination of 1,3-benzenedimethanamine in food simulants*

Part 13: *Determination of 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A) in food simulants*

Part 14: *Determination of 3,3-bis(3-methyl-4-hydroxyphenyl)-2-indoline in food simulants*

Part 15: *Determination of 1,3-butadiene in food simulants*

Part 16 *Determination of caprolactam and caprolactam salt in food simulants*

Part 17: *Determination of carbonyl chloride in plastics*

Part 18: *Determination of 1,2-dihydroxybenzene, 1,3- dihydroxybenzene, 1,4- dihydroxybenzene, 4,4'-dihydroxybenzophenone and 4,4'dihydroxybiphenyl in food simulants*

Part 19: *Determination of dimethylaminoethanol in food simulants*

Part 20: *Determination of epichlorohydrin in plastics*

Part 21: *Determination of ethylenediamine and hexamethylenediamine in food simulants*

Part 22: *Determination of ethylene oxide and propylene oxide in plastics*

Part 23: *Determination of formaldehyde and hexamethylenetetramine in food simulants*

Part 24: *Determination of maleic acid and maleic anhydride in food simulants*

Part 25: *Determination of 4-methyl-pentene in food simulants*

Part 26: *Determination of 1-octene and tetrahydrofuran in food simulants*

Part 27: *Determination of 2,4,6-triamino-1,3,5-triazine in food simulants*

Part 28: *Determination of 1,1,1-trimethylopropane in food simulants*

Parts 1 to 8 are European Standards.

Parts 9 to 28 are Technical Specifications, prepared within the Standards, Measurement and Testing project, MAT1-CT92-0006, "*Development of Methods of Analysis for Monomers*".

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Introduction

Isocyanates, characterised by the -NCO group, are monomers used for the manufacture of materials and articles intended to come in contact with food. During manufacture residual isocyanates can remain in the polymer and can migrate into food coming into contact with the polymer.

1 Scope

This part of this European Standard describes a method for the determination of individual and total levels of residual isocyanates in plastics materials and articles.

This method is applicable to the analysis of polyurethane polymers. The total level of isocyanate monomers in materials and articles determined according to the procedure described in this standard is given in milligrams of NCO per kilogram of material or article. The method is capable of quantitative determination of individual isocyanates measured as NCO at 0,04 mg/kg and total isocyanates at 1,0 mg/kg.

NOTE The method has been applied to the analysis of 9 isocyanate monomers listed in 3.1. It has not been applied to the analysis of octadecyl isocyanate, diphenylether-4,4'-diisocyanate or 3,3'-dimethyl-4,4'-diisocyanatobiphenyl as samples of these monomers have not been obtained. There is no reason to anticipate that the method may not be suitable for the analysis of these monomers also.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 13130-1:2004, *Materials and articles in contact with foodstuffs - Plastics substances subject to limitation - Part 1: Guide to test methods for the specific migration of substances from plastics to foods and food simulants and the determination of substances in plastics and the selection of conditions of exposure to food simulants.*

3 Principle

The procedure consists of two parts: screening and, if necessary, quantitative determination. Quantitative determination is applied only if isocyanates are detected by the screening procedure.

Materials and articles are initially screened for residual isocyanates by solvent extraction with dichloromethane and concurrent derivatization with 9-(methylaminomethyl)anthracene. 1-Naphthyl isocyanate is used during the screening procedure to check that the derivatization procedure has been successful. The resultant fluorescent derivatives are analysed by high performance liquid chromatography with fluorescence detection.

Materials found to contain residual isocyanates are quantified by standard addition to the material or article under test, using 1-naphthyl isocyanate as internal standard.

If interferences are experienced with the internal standard then calibration is carried out by standard addition omitting the internal standard, as described in annex A.

Confirmation of isocyanate levels is carried out by re-analysing the sample extracts on an HPLC column with different elution characteristics.

4 Reagents

WARNING: All chemicals are hazardous to health to a greater or lesser extent. It is beyond the scope of this standard to give instructions for the safe handling of all chemicals, that meet, in full, the legal obligations in all countries in which this standard may be followed. Therefore, specific warnings are

not given and users of this standard shall ensure that they meet all the necessary safety requirements in their own country.

NOTE 1 Isocyanates react extremely rapidly with moisture. Suitable precautions should be taken to ensure all glassware is dry. All laboratory glassware should be rinsed with diethyl ether (4.2.2) and baked at 105 °C overnight before use. After baking, vials should be placed in a desiccator and stored until required. Isocyanate standards should be protected from moisture and stored under refrigeration at -20 °C.

NOTE 2 All reagents should be of recognised analytical quality, unless otherwise specified.

4.1 Analytes

4.1.1 2,6-toluene diisocyanate $CH_3C_6H_3(NCO)_2$

4.1.2 diphenylmethane-4,4'-diisocyanate $OCNC_6H_4CH_2C_6H_4NCO$

4.1.3 2,4-toluene diisocyanate $CH_3C_6H_3(NCO)_2$

4.1.4 hexamethylene diisocyanate $OCNC_6H_{12}NCO$

4.1.5 cyclohexyl isocyanate $C_6H_{11}NCO$

4.1.6 1,5-naphthalene diisocyanate $C_{10}H_6(NCO)_2$

4.1.7 diphenylmethane-2,4'-diisocyanate $OCNC_6H_4CH_2C_6H_4NCO$

4.1.8 2,4-toluene diisocyanate dimer

4.1.9 phenyl isocyanate C_6H_5NCO

4.1.10 1-naphthyl isocyanate (internal standard, $C_{10}H_7NCO$), which contains no impurity at > 1 % by area which will elute at the same retention time as any of the nine individual isocyanate derivatives.

All standards should be of > 99 % purity.

4.2 Reagents

4.2.1 Dichloromethane (DCM, CH_2Cl_2), < 30 ppm H_2O, containing no impurity at > 1 %, by area, which elutes at the same HPLC retention time as the isocyanate derivatives or internal standard derivative peaks. DCM should be dried over a bed of molecular sieve (5 Å) for 24 h prior to use.

4.2.2 Diethylether ($(C_2H_5)_2O$), at least 99 % purity.

4.2.3 9-(Methylaminomethyl)anthracene (MAMA, $CH_3NHCH_2C_{14}H_9$), containing no impurity at > 1 %, by area, which elutes at the same HPLC retention time as the isocyanate derivatives or internal standard derivative peaks.

4.2.4 N,N'-Dimethylformamide ($HCON(CH_3)_2$), containing no impurity at > 1 %, by area, which elutes at the same HPLC retention time as the isocyanate derivatives or internal standard derivative peaks.

4.2.5 Individual stock standard solutions (1000 µg/ml)

Weigh 0,01 g of isocyanate standard (4.1), to an accuracy of 0,1 mg, in a 10 l volumetric flask. Rapidly make-up to the mark with DCM (4.2.1) and shake thoroughly. Ultrasonification may be used as an aid to dissolution. Repeat the procedure to provide a second stock solution.

4.2.6 Individual intermediate standard solutions (100 ug/ml)

Put approximately 5 ml DCM (4.2.1) into a 10 ml volumetric flask. Using a 1000 µl syringe, dispense 1000 µl of stock solution (4.2.5) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly. Repeat the procedure using the second stock solution (4.2.5) to provide a second intermediate standard solution.

4.2.7 Individual dilute standard solutions (1 µg/ml)

Put approximately 5 ml DCM (4.2.1) in a 10 ml volumetric flask. Using a 100 µl syringe, dispense 100 µl of intermediate standard solution (4.2.6) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly.

NOTE Individual dilute standard solutions should be prepared for each isocyanate (4.1).

4.2.8 Internal standard stock solution (1000 µg/ml)

Weigh 0,01 g of 1-naphthyl isocyanate (4.1.10), to an accuracy of 0,1 mg, into a 10 ml volumetric flask. Rapidly make-up to the mark with DCM (4.2.1) and shake thoroughly. Ultrasonification may be used as an aid to dissolution.

4.2.9 Intermediate internal standard solution (100 µg/ml)

Put approximately 5 ml DCM (4.2.1) in a 10 ml volumetric flask. Using a 1000 µl syringe, dispense 1000 µl of internal standard stock solution (4.2.8) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly.

4.2.10 Dilute internal standard solution (1 µg/ml)

Put approximately 5 ml DCM (4.2.1) in a 10 ml volumetric flask. Using a 100 µl syringe, dispense 100 µl of intermediate internal standard solution (4.2.9) into the flask, ensuring that the syringe needle tip is immersed into the DCM before dispensing. Make-up to the mark with DCM and shake thoroughly.

NOTE Stock and standard solutions (4.2.5 to 4.2.10) should be stored with the exclusion of light and moisture at - 20 °C. They are stable for up to 1 month under these conditions.

4.2.11 Derivatization reagent solution (0,26 mg/ml)

Weigh 0,013 g of MAMA (4.2.3), to an accuracy of 0,1 mg, into a 50 ml volumetric flask. Make-up to the mark with DCM (4.2.1) and shake thoroughly.

NOTE Derivatization reagent should be prepared fresh daily, because of the photo-instability of MAMA, and stored with the exclusion of light.

4.2.12 Derivative dissolution solvent

Using a measuring cylinder, dispense 50 ml N,N'-dimethylformamide (4.2.4) into a 100 ml volumetric flask, make-up to the mark with the requisite HPLC mobile phase (7.1.5.1) and mix thoroughly.

4.2.13 Preparation of individual isocyanate derivatives for HPLC peak assignment

Using a 100 µl syringe, dispense 100 µl of dilute isocyanate standard solution (4.2.7) into a vial (5.4). Using a 1 ml syringe dispense 1 ml of derivatization reagent solution (4.2.11) into the same vial. Cap, gently agitate to mix the contents, and allow to stand for 60 min with the exclusion of light. Evaporate the vial contents to dryness under a stream of nitrogen, add 10 ml derivative dissolution solvent (4.2.12) and mix thoroughly. Ultrasonification may be used as an aid to dissolution.

Repeat for each isocyanate, using the individual dilute solutions (4.2.7).

NOTE Derivative solutions should be stored with the exclusion of light at ambient temperature. They are stable for up to two weeks under these conditions.

Repeat the procedure with the dilute internal standard solution (4.2.10).

5 Apparatus

5.1 General

An instrument or piece of apparatus is mentioned only if it is special, or made to particular specifications. Usual laboratory equipment is assumed to be available.

NOTE The MAMA-isocyanate derivatives are not sensitive to moisture and so glassware used for operations involving the derivatives need not be especially dried before use.

5.2 High performance liquid chromatograph, equipped with a fluorescence detector

Excitation Wavelength - 254 nm

Emission Wavelength - 412 nm

5.3 Chromatographic column

The column has to permit the separation of each of the MAMA derivatives of the nine individual isocyanates from one another as well as from that of the MAMA derivative of the internal standard. The peaks of the isocyanate standard derivatives and that of the internal standard derivative shall not overlap by more than 1 % of peak area with each other and with peaks resulting from other compounds.

The following are examples of HPLC columns found suitable for analysis of isocyanate derivatives:

a) 250 mm x 4,6 mm stainless steel column packed with silica, 5 µm particle size, 80 Å pore size, 220 m²/g surface area, octadecyl silyl bonded phase, 7 % carbon loading, partially end-capped;

b) 125 mm x 3,0 mm stainless steel columns packed as for a);

c) 250 mm x 4,6 mm stainless steel column packed with silica, 5 µm particle size, 120 Å pore size, 200 m²/g surface area, octadecyl silyl bonded phase, 11 % carbon loading, end-capped;

d) 250 mm x 4,0 mm stainless steel column packed as for c);

e) 125 mm x 4,0 mm stainless steel column packed with silica 5 µm particle size, 60 Å pore size, 220 m²/g surface area, octasilyl bonded phase, 11,5 % carbon loading, partially end-capped.

5.4 Glass vials

20 ml capacity with polytetrafluoroethylene-faced butyl rubber septa and aluminium crimp caps. Vials should be rinsed with diethyl ether (4.2.2), baked at 105 °C overnight and then stored in a desiccator until required for use.

NOTE Erlenmayer flasks, with a capacity of 25 ml, with ground glass joints can be used instead of 20 ml vials. They should be washed, dried and stored as for glass vials.

5.5 Glass sample vials suitable for the HPLC system employed.

5.6 Glass barrel syringes with needles, of 5 µl, 10 µl, 50 µl, 100 µl, 250 µl, 500 µl and 1000 µl capacities.

6 Samples

The laboratory samples of polymer materials or articles, to be analysed are obtained and stored as described in EN 13130-1.

The samples of plastics to be analysed have to be representative of the material, or article, presented for